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AND HYDRIODIC ACIDS, BY S. DUSHMAN**

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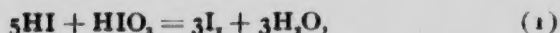
THE RATE OF THE REACTION BETWEEN IODIC AND HYDRIODIC ACIDS

BY SAUL DUSHMAN

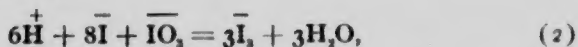
In 1888 the rate of reaction between iodic and hydriodic acids was made the subject of a research by O. Burchard,¹ who endeavored to discover a relation between the rate and the concentrations of these two reagents. His results, however, were unsatisfactory, and the author concludes his paper with the words, "In spite of all attempts, I have not succeeded in representing the rate of the reaction by a general differential equation".

In light of the electrolytic dissociation theory introduced by Arrhenius just at the time of Burchard's publication, it now seems advisable to represent hydrogen iodide in solution as consisting almost entirely of hydrion (H^+) and iodion (I^-); similarly a solution of iodic acid contains hydrion (H^+) and iodation (IO_3^-), while brown "iodine" solution contains tri-iodion (I_3^-).

Thus, in place of Burchard's equation,



it seems better to write



and in consequence, I have studied the effect of the concentrations of H^+ , I^- , IO_3^- and I_3^- on the rate, instead of adopting the variables chosen by Burchard.

In planning the experiments, I adopted a method which was originally employed by Harcourt and Esson in their classical research, "On the Observation of the Course of Chemical Change", in 1866,² but which had, apparently been completely forgotten by 1888. The principle of the method is very sim-

¹ Zeit. phys. Chem. 2, 796 (1888).

² Jour. Chem. Soc. 20, 476 (1867).

ple, and consists in keeping the concentrations of all the reagents but one constant, or almost constant, during the progress of the reaction; any change in the rate must then be ascribed to changes in the concentration of that one substance only. In Burchard's work on the other hand, the concentrations of all the reagents changed during every experiment, and he was unable to discover the effect due to each.

In the investigations of Harcourt and Essen, and in those carried on in this laboratory by Messrs. Bray,¹ Bell,² Roebuck,³ DeLury,⁴ Forster,⁵ and Miss Benson,⁶ the concentrations of all the reagents except one were *held constant by employing relatively high concentrations of the reagents in question*. In my preliminary experiments I made up the solutions on the same plan, using a small amount of potassium iodate (iodation), and large excesses of potassium iodide (iodion) and hydrochloric acid (hydrion). I soon found, however, that the solutions had to be much diluted in order to make the rate of the reaction slow enough to measure, and that in these very dilute solutions accurate analytical determination of the iodine liberated was impossible.

Finally I replaced the excess of hydrochloric acid by excess of acetic acid and sodium acetate, thus obtaining solutions in which *the concentration of the hydrion, though lower than those of the iodation and iodion, remained unaltered* throughout the experiment. In the acetic acid solutions the rate was much slower than in those containing hydrochloric acid, great dilution was not necessary, and the analytical difficulties referred to above were avoided.

Experiments in which the concentrations of the reagents were systematically varied led to very simple results, namely, that the rate of the reaction between hydriodic and iodic acids

¹ Jour. Phys. Chem. 7, 92 (1903).

² Ibid. 7, 61 (1903).

³ Ibid. 6, 365 (1902).

⁴ Ibid. 7, 239 (1903).

⁵ Ibid. 7, 640 (1903).

⁶ Ibid. 7, 1 (1903).

is proportional to the concentration of the iodation, to the square of the concentration of the hydrion, and to the 1.8th or 1.9th power of that of the iodion, while the tri-iodion exerts an accelerating influence which was studied in detail. By means of the differential equation embodying these relations, I was able to predict the course of the reaction in solutions containing hydriodic and iodic acids only.

The results, apart from their intrinsic interest, are of value as showing the power of Harcourt and Esson's method in the study of Chemical Kinetics. As recently as 1898, in a paper on "The Reduction of Bromic Acid and the Law of Mass Action",¹ the authors, Messrs. Judson and Walker, expressed themselves as follows: "It is evident, therefore, that the action of hydriodic acid on the oxygen acids of the halogens is too intricate a nature to give any satisfactory numerical results". The rate of this "intricate reaction" is now known as a simple function of the concentrations of the reagents involved.

METHOD OF WORKING

Precautions taken to exclude air

As the unsatisfactory outcome of Burchard's investigation has been ascribed in part to the action of atmospheric oxygen on his solutions, I took special precautions to exclude air during the work. Pairs of experiments, however, in one of which the air was excluded, while in the other it was allowed access, seemed to show that the error arising from this source was negligible.

All the solutions used in the experiments were prepared free from air by boiling and cooling in vacuo, and were kept under carbonic acid gas, which was purified by passing through water, solutions of sulphuric acid, ferrous sulphate, and permanganate of potassium, and through a long tube filled with cotton wool.

Before removing a solution from one of the stoppered flasks clamped in the thermostat (see below), the pipettes were filled

¹ Jour. Chem. Soc. 73, 411 (1898).

with carbon dioxide, and a current of the gas was passed into the flask as long as the stopper was out.

Description of an experiment

The main stock of the solutions of potassium iodide, potassium iodate, acetic acid and sodium acetate was kept in bottles under carbon dioxide, as already stated; and before each series of experiments about 200 cc of each were brought to 0° C in stoppered flasks (clamped in the thermostat) from which the air had been removed by a current of carbon dioxide. The thermostat was also provided with a large test-tube (100 cc capacity) and a 500 cc beaker with stirring rod.

Each measurement contained in the following tables involved the preparation of a new reacting mixture, as follows: Into the test-tube was first pipetted air-free water in quantity sufficient (together with that of the reagents subsequently added) to make up the total volume to 100 cc; measured quantities of sodium acetate, acetic acid and potassium iodide solutions were then added. The potassium iodate was measured into the beaker and the stirrer set in motion, the contents of the test-tube were then thrown in, and at the same instant the catch of a stop-watch was released by means of a pedal. Experiments with colored solutions showed that a homogeneous mixture was attained in from one-fifth to one-half second. When it was desired to interrupt the reaction, the contents of the beaker were again stirred rapidly, about 10 cc of ammonium bicarbonate solution thrown in from a test-tube and the watch stopped. The iodine liberated was then determined with centinormal sodium arsenite and iodine solutions, using starch as an indicator.¹ Duplicate experiments gave results agreeing within 0.10 cc of the volumetric arsenite solution, while duplicate analyses of the same mixture agreed within 0.05 cc.

All pipettes and burettes used in these measurements were freshly calibrated, the pipettes by weighing the distilled water discharged at 4° C, and the burettes as described in Ostwald's

¹ For the method of analysis of the mixture in presence of excess of iodine, see page 468.

"Hand- und Hilfsbuch," page 103. In using the pipettes 45 seconds were allowed for draining.

Solutions employed

Water. — All the water used in these experiments was freed from air, and kept under carbon dioxide.

Potassium iodate. — 0.00918-F,¹ and 0.00100-F KIO_3 , prepared by dissolving weighed quantities of the salt, and standardized by decomposing a measured volume with excess of potassium iodide and hydrochloric acid, adding excess of ammonium bicarbonate, and titrating with 0.01049-N sodium arsenite.

Sodium acetate. — 0.10035-F, $\text{C}_2\text{H}_3\text{O}_2\text{Na}$, prepared by dissolving 13.6 grams of Merck's crystallized sodium acetate to one liter; a few crystals of menthol were added to prevent the growth of moulds. To standardize a measured volume was evaporated in a tared crucible at 100°C , the crucible and salt were then heated to 110° – 120° for four hours, allowed to cool in a desiccator, and the anhydrous sodium acetate weighed.

Acetic acid. — 1.147-F, $\text{C}_2\text{H}_4\text{O}_2$, prepared by diluting Merck's "pure glacial acetic acid, 99.5 percent acid", and titrating against standard potash.

Hydriodic acid. — 0.1128-F and 0.001132-F HI; prepared by diluting a stock solution made from water, iodine, and red phosphorus; titrated against the standard potash. These solutions contained a little free iodine, which was determined by sodium arsenite (20 cc of the 0.1128-F HI took 0.42 cc of 0.0105-N arsenite), and in each measurement in which hydriodic acid was used, the small correction for the free iodine was made at the time of the analysis.

Iodic acid. — 0.00976-F and 0.00100-F HIO_3 . Large, colorless crystals of iodic acid, free from sulphuric acid (prepared by oxidizing iodine with nitric acid, sp. gr. 1.53) were dissolved, and the solutions standardized by sodium arsenite (see under Potassium iodate).

Iodine and potassium iodide. — Twenty-five cc was equiva-

¹ Formula-weights per liter.

lent to 21.77 cc 0.1049-N arsenite, hence 0.04567-F tri-iodion, I_3^- . After boiling off the free iodine, 50 cc with silver nitrate gave 1.1387 g AgI, hence 0.0970-F KI. Since each mol of iodine (I_2) reacts with one of potassium iodide (iodion, I^-) to form one of potassium tri-iodide (tri-iodion, I_3^-) the formation of 0.04567 mol I_3^- per liter has used up 0.04567 mol iodion, leaving $0.0970 - 0.04567 = 0.05133$ mol iodion (I^-) per liter.

Iodine and hydriodic acid.—The 0.1128-F hydriodic acid was saturated with iodine, and the "free iodine" (tri-iodion) determined by sodium arsenite and found to be 0.0415-F I_3^- . Subtracting 0.0415 from 0.1128 there remains the concentration of the iodion, 0.0713-F, while the hydrion is 0.1128-F H^+ .

Volumetric sodium arsenite.—0.01049-normal; standardized with dry, freshly sublimed iodine. The *volumetric iodine solutions* were compared daily with the arsenite; and the *volumetric sodium thiosulphate* was standardized against the iodine solutions.

The half saturated *ammonium bicarbonate* solution was kept under CO_2 . A distinct blue coloration was obtained when one drop of centinormal iodine was added to a mixture of 100 cc water, 10 cc ammonium bicarbonate solution, 2 cc starch solution, and a few drops of normal potassium iodide.

RESULTS OF THE EXPERIMENTS

Explanation of the Tables (Series I and II)

At the head of each table is given the initial composition of the reacting mixture. The numbers following each formula denote the number of gram-formula-weights of that reagent in 100 cc of reacting mixture. Thus IO_3^- , 0.000025; I^- , 0.00177; HAc, 0.00585; NaAc, 0.0015 (at the head of Table I) means that 25 cc of 0.0010-F KIO_3 , 20 cc of 0.0885-F KI, 5 cc of 1.17-F HAc, 15 cc of F/10 NaAc were made up to a volume of 100 cc. From the numbers after HAc and NaAc, was calculated the quantity of hydrion, H^+ , in the mixture, assuming the dissocia-

tion constant of acetic acid to be 0.000018,¹ and the sodium acetate to be totally dissociated; thus for HAc 0.00585, and NaAc 0.0015 (V 0.1 liter).

$$KV(\text{HAc}) = \overset{+}{\text{H}} \times \overline{\text{Ac}}$$

$$0.000018 \times 0.1 \times 0.00585 = \overset{+}{\text{H}} \times (\overset{+}{\text{H}} + 0.0015),$$

whence $\overset{+}{\text{H}} = 0.000007$

Under "*t*" is entered the time in minutes during which the mixture was allowed to react, and under "*As*" the number of cc of the volumetric sodium arsenite equivalent to the iodine liberated. In the third column are entered the values k_1 or k_2 .

$$k_1 = \frac{1}{t} \log_{10} \frac{IO_3}{IO_3 - x}, \dots\dots\dots (I)$$

$$k_2 = \frac{1}{t} \left(\frac{1}{I - y} - \frac{1}{I} \right) \dots\dots\dots (II)$$

To obtain x , the number of mols of IO_3 reduced for each cc of *As*, the burette readings must be multiplied by 0.00000175. (1 cc *As* = 0.00001049 equivalent; 1 mol IO_3 gives 6 equivalents of iodine.)

To obtain y , the number of moles of $\bar{I}$ corresponding to 1 cc of *As* in the titration, the burette readings must be multiplied by 0.00001398. (From equation (2))

8 KI yields 3 KI_3 = 6 equivalents of iodine,

or for each mol of KI destroyed, $3/8$ mol of KI_3 is formed, that is, $3/4$ equivalent of *As* is used in titration. Hence, 1 cc *As* = $4/3 \times 1/1000 \times 0.01049 = 0.00001398$ mol KI.)

SERIES I. ACETIC ACID SOLUTIONS, POTASSIUM IODATE PRESENT IN SMALL QUANTITY

Effect of Iodation

The constancy of k_1 in each of the tables of this series shows that the rate is proportional to the concentration of the potassium iodate (iodation) in the reacting mixture. This conclusion is confirmed by the fact that doubling the concentration

¹ From the data and formulas of Arrhenius' paper (Zeit. phys. Chem. 4, 106) it appears that at 0° C the dissociation constant of acetic acid is below 0.000017. The hydron concentrations given at the heads of Tables 1-27 are therefore all somewhat too high. See, however, page 474.

of the iodate does not affect k , (Tables 2 and 1). The slight falling off of k in Table 2 is to be expected, as the concentration of the iodide is in relatively small excess.

Effect of Hydrion

From a comparison of Tables 1 and 3, and 1 and 4, it is apparent that the rate is proportional to the square of the concentration of the hydrion. In the first pair, the concentration of the hydrion was changed by doubling the concentration of the acetic acid, and in the second pair by doubling that of the sodium acetate. In Table 5 the concentration of both acid and salt is double that in Table 1, but the rate remains the same, thus affording a striking confirmation of the view that it is the concentration of hydrion that is effective.

Effect of Iodion

The effect of the concentration of iodion is not quite so simple. From Tables 1 and 6, 7 and 4, it is seen that doubling the concentration of the potassium iodide (iodion) multiplies the rate by $2^{1.85}$ or $2^{1.9}$. From Tables 9 and 10 we see that varying the concentration of iodion from 0.00886 to 0.000886 mol per liter, does not cause any variation in the exponent. It can, however, be seen from Table 10, and it will be more apparent from Series II, that the lower the concentration of iodion, the nearer the proportionality is between the rate and the square of its concentration. The other tables of this series show that the effects of the acid, acetate, and iodide are each independent of the others as well as of the iodate.

TABLE 1

IO_3 , 0.000025; I , 0.00177; HAc , 0.00585; NaAc , 0.0015;
 H , 0.0000070

t	As	$k_1 \times 10^3$
2	1.13	17.9
4	2.24	18.5
6	3.15	18.0
8	4.15	18.6
10	4.87	18.6
		Av. 18.3

TABLE 2

IO_3 , 0.000050; I , 0.00177; HAc , 0.00585; NaAc , 0.0015;
 H , 0.000007

t	As	$k_1 \times 10^3$
2	2.20	17.4
2	2.26	17.9
4	4.04	16.8
6	6.09	17.3
8	7.24	15.8
		Av. 17.3

TABLE 3

IO_3 , 0.000025; I , 0.00177; HAc , 0.0117; NaAc , 0.0015;
 H , 0.000014

t	As	$k_1 \times 10^3$
1	2.30	76.2
2	4.17	75.0
2	4.14	74.4
2.5	4.78	71.0
4	6.87	71.2
6	8.76	68.7
		Av. 72.6

TABLE 4

IO_3 , 0.000025; I , 0.00177; HAc , 0.00585; NaAc , 0.0030;
 H , 0.0000035

t	As	$k_1 \times 10^3$
2	0.34	5.3
4	0.62	4.8
6	0.89	4.7
8.5	1.22	4.6
10	1.54	4.9
		Av. 4.8

TABLE 5

IO_3 , 0.000025 ; I , 0.00177 ; HAc , 0.0117 ; NaAc , 0.0030 ;
 H , 0.000007

t	As	$k_1 \times 10^3$
2	1.22	19.4
4	2.27	18.8
6	3.21	18.4
8	4.35	19.7
		Av. 19.1

TABLE 6

IO_3 , 0.000025 ; I , 0.00354 ; HAc , 0.00585 ; NaAc , 0.0015 ;
 H , 0.000007

t	As	$k_1 \times 10^3$
2	3.86	68.4
3	5.16	64.8
4	6.50	65.9
6	8.18	61.5
8	9.62	60.7
		Av. 64.3

TABLE 7

IO_3 , 0.000025 ; I , 0.00354 ; HAc , 0.00585 ; NaAc , 0.0030 ;
 H , 0.0000035

t	As	$k_1 \times 10^3$
2	1.17	18.5
4	2.19	18.1
6	3.20	18.3
8	3.93	17.5
10	4.78	17.6
		Av. 18.0

TABLE 8

IO₃, 0.000025; I, 0.00354; HAc, 0.0117; NaAc, 0.0015;
H, 0.000014

t	As	$k_1 \times 10^3$
1	6.03	236.0
1.5	7.96	235.8
1.75	8.89	241.5
2	9.54	239.0
		Av. 238.2

TABLE 9

IO₃, 0.000025; I, 0.00885; HAc, 0.00585; NaAc, 0.0015;
H, 0.000007

t	As	$k_1 \times 10^3$
1	8.64	403.2
1.25	9.66	391.5
1.50	10.46	381.2
1.75	11.24	383.4
		Av. 389.8

TABLE 10

IO₃, 0.000025; I, 0.000885; HAc, 0.00585; NaAc, 0.0015;
H, 0.000007

t	As	$k_1 \times 10^3$
2	0.32	4.9
4	0.57	4.4
6	0.96	5.0
8	1.25	5.0
10	1.45	4.6
		Av. 4.8

**SERIES II. ACETIC ACID SOLUTIONS, POTASSIUM IODIDE
PRESENT IN SMALL QUANTITY**

Effect of Iodion

The constancy of k_2 in each of the tables of this series shows that the effect of iodion varies as the square of its concentration when it is present in small quantity relatively to the iodate. In confirmation of this conclusion, we find that Table 12, in which the concentration of the iodide (iodion) is doubled, gives approximately the same constant as Table 11.

Effect of Iodation

Table 13 shows that doubling the concentration of the potassium iodate (iodation) multiplies the rate by 2; hence, as in Series I, the rate varies with the first power of the concentration of the iodation.

Effect of Hydrion

Tables 11 and 14, and 11 and 15, show that halving or doubling the concentration of the hydrion multiplies the rate by $\frac{1}{4}$ or 4 respectively. Tables 11 and 16 show that if the concentration of both acid and acetate be doubled, the rate remains unchanged. Hence, as in Series I, the rate is proportional to the second power of the concentration of the hydrion.

TABLE 11

IO₃, 0.000225; I, 0.00018; HAc, 0.0117; NaAc, 0.0015;
H, 0.000014

<i>t</i>	<i>As</i>	<i>k₂</i>
4	1.06	125
6	1.46	120
8	1.84	116
12	2.69	122
15	3.07	116
		—
		Av. 120

TABLE 12

IO_3 , 0.000225 ; I , 0.00036 ; HAc , 0.0117 ; NaAc , 0.0015 ;
 H , 0.000014

t	As	k_1
1	1.04	119
2	1.86	109
3	2.72	110
4	3.46	108
		Av. 112

TABLE 13

IO_3 , 0.00045 ; I , 0.00018 ; HAc , 0.0117 ; NaAc , 0.0015 ;
 H , 0.000014

t	As	k_1
2	0.99	232
3	1.44	233
4	1.92	241
6	2.60	234
8	3.14	227
		Av. 235

TABLE 14

IO_3 , 0.000225 ; I , 0.00018 ; HAc , 0.0117 ; NaAc , 0.0030 ;
 H , 0.000007

t	As	k_1
16	1.10	33
24	1.45	29
		Av. 31

TABLE 15

IO_3 , 0.000225 ; I , 0.00018 ; HAc , 0.0234 ; $NaAc$, 0.0015 ;
 H , 0.000028

t	As	k_1
2	1.64	406
3	2.43	452
4	3.05	432
		Av. 442

TABLE 16

IO_3 , 0.000225 ; I , 0.00018 ; HAc , 0.0234 ; $NaAc$, 0.0030 ;
 H , 0.000007

t	As	k_1
4	1.10	130
6	1.45	120
8	1.73	108
12	2.58	112
		Av. 117

Representation of the results by a differential equation

The results of the measurements of Series I and II may thus be stated in the following words :

"The rate of the reaction between iodation, iodion, and hydrion, is proportional to the first power of the concentration of the iodation, to the 1.85th to second power of that of the iodion, and to the second power of the concentration of the hydrion."

Or, expressed in the form of a differential equation,

$$\frac{dx}{dt} = K \left(\frac{IO_3 - x}{V} \right) \left(\frac{I - y}{V} \right)^{1.85} \left(\frac{H}{V} \right)^2 \dots\dots\dots (A)$$

where $y = 8x$, and V is the volume in liters.

From the definitions of k_1 and k_2 on page 19, it follows that

$$K = 2.303 k_1 V^3 (I)^{1.85} (H)^2 \dots\dots\dots (B)$$

$$K = k_2 V^3 (IO_3) (H)^2 \dots\dots\dots (C)$$

The following table contains the value of K for each of the foregoing tables, calculated by means of equations (B) and (C). Its constancy is a measure of the accuracy of equation (A). Physically interpreted, K represents the calculated number of mols of iodate that should be reduced in one minute when 1 mol of potassium iodide, 1 mol iodate, and 1 mol hydriodion were present in a volume of 1 liter.

TABLE 17

Nu.	$IO_3 \times 10^3$	$I \times 10^3$	$H \times 10^3$	3303 k_1	k_2	$K \times 10^{-10}$
1	25	177	7.0	42	—	2.47
2	50	177	7.0	39	—	2.30
3	25	177	14.0	167	—	2.46
4	25	177	3.5	11	—	2.59
5	25	177	7.0	44	—	2.59
6	25	354	7.0	138	—	2.34
7	25	354	3.5	41	—	2.59
8	25	354	14.0	548	—	2.12
9	25	885	7.0	896	—	2.47
10	25	89	7.0	11	—	2.59
11	225	18	14.0	—	120	2.73
12	225	36	14.0	—	112	2.56
13	450	18	14.0	—	235	2.70
14	225	18	7.0	—	31	2.82
15	225	18	28.0	—	442	2.55
16	225	18	14.0	—	117	2.68

Av. 2.54

SERIES III. ACETIC ACID SOLUTIONS, IODINE (TRI-IODION) PRESENT IN EXCESS

It is obvious, that owing to the excess of iodine put into the reacting mixture, it was not possible to make up solutions in which the quantity of potassium iodide was relatively small. Consequently in all the experiments of the present series the potassium iodate was selected as the substance to be present in small quantity.

In the measurements of this series a measured volume of decinormal iodine solution was mixed with the potassium iodate in the beaker (see "Description of an experiment," p. 456), and

water was added to bring the total volume up to 100 cc. Owing to the fact that the iodine liberated during the reaction was very small in amount compared with that initially present, the progress of the reaction was followed by estimating the residual potassium iodate instead of by trying to determine the small increase in the free iodine. The method has been worked out by Mr. Forster.¹

Method of Analysis

The reaction was stopped by throwing in the ammonium bicarbonate, as before; sodium arsenite solution (0.1049-N) was run in from a burette, and then a little starch solution to determine the end-point. Thrice normal hydrochloric acid was next added in quantity sufficient to neutralize the sodium acetate, the ammonium bicarbonate, and the volumetric sodium arsenite, and to leave an excess of 2 cc of the 3-N hydrochloric acid. In solutions of this degree of acidity the potassium iodate was immediately reduced with liberation of an equivalent quantity of iodine, which was then determined by 0.01054-N sodium thiosulphate.

Blank experiments showed that the results are accurate within 0.10 cc (two drops of the volumetric sodium thiosulphate solution), but it is necessary to complete the titration within five minutes or iodine will be liberated by the action of the arsenic acid formed from the volumetric arsenite.

Explanation of the Tables

The symbols IO_3 , HAc , $NaAc$, H , I , t , k_1 ,² have the meanings assigned on page 458. After KI is given the number of mols of potassium iodide, and after "Iod" the number of cc of the iodine solution added in making up the reacting mixture. In the brackets are given the number of mols iodion ($\bar{I}$) and triiodion ($\bar{I}_3$) contained in the iodine solution. The total quantity of iodion present in the reacting mixture is thus the sum of the

¹ Jour. Phys. Chem. 7, 640.

² In the tables of this series k_1' has been written instead of k_1 , to distinguish the tables of this series from those of Series I.

numbers after KI and I. Under "Th" is given the number of cc of 0.01034-N sodium thiosulphate solution equivalent to the iodine liberated from the residual potassium iodate. In order to obtain $IO_3 - x$, used in calculating k_1' , these burette readings must be multiplied by 0.000001744.

Effect of Iodation

From the constancy of k_1' in each of the tables of this series and by comparing Tables 20 and 23 (in the latter of which the concentration of the potassium iodate was double that in the former) it is apparent that the rate is proportional to the first power of the concentration of the iodation, and that the law according to which the iodation affects the rate is not modified by the presence of tri-iodion.

Effect of Hydriion

By comparing Tables 20, 22 and 25 it is evident that the rate is proportional to the square of the concentration of the hydriion. Thus the law according to which the hydriion affects the rate is not modified by the presence of tri-iodion.

Effect of Tri-iodion and of Iodion

The effect of tri-iodion might have been determined by comparing the experiments of this series with others in which the composition of the reacting mixture was the same except as regards the tri-iodion. Instead of undertaking a new series of measurements for this purpose, however, I have utilized those of Series I, making a correction for the small difference in the concentration of the iodion by assuming that k_1 is proportional to the 1.9th power of the concentration of the iodion (see page 460). In Table 18 are entered the compositions of the solutions of Tables 19 to 27, and the values of k_1' ; also under k_1 the constants from the corresponding tables of Series I, corrected as described. The difference $k_1' - k_1$, which expresses the effect of tri-iodion on the rate, is roughly proportional to the concentration of the tri-iodion, to somewhat more than the second power of that of the hydriion, and to slightly less than the first power of the iodion.

TABLE 18

No.	$IO^3 \times 10^3$	$I \times 10^3$	$H \times 10^3$	$I_2 \times 10^3$	$k_1' \times 10^3$
19	25	2053	7.0	183.0	38.6
20	25	1911	7.0	91.5	27.6
21	25	1841	7.0	45.7	23.6
22	25	1911	14.0	91.5	121.4
23	50	1911	7.0	91.5	29.1
24	25	3682	7.0	91.5	79.5
25	25	1911	3.5	91.5	7.3
26	25	3611	7.0	45.7	72.1
27	25	3820	7.0	183.0	97.2

No.	$k_1 \times 10^3$	$\frac{k_1' - k_1}{\times 10^3}$	Q	$k_1' \times 10^3$ calc.	Diff.
19	24.3	14.3	7.8	37.3	- 3.4 %
20	20.8	6.8	7.9	27.3	- 1.1
21	19.8	3.8	9.0	22.9	- 1.7
22	82.8	38.6	(12.5)	108.8	-10.0
23	19.7	9.4	(10.9)	26.2	-10.0
24	69.3	10.2	6.2	81.8	+ 4.0
25	5.5	1.8	7.8	7.1	- 3.0
26	66.7	5.4	6.7	72.8	+ 1.0
27	74.3	22.9	6.7	100.3	+ 3.0

Av. 7.4

The quotient,

$$Q = \frac{(k_1' - k_1) V^4 \times 10^{-3}}{(I_2) \times (H)^2 \times (I)}$$

is thus approximately constant, the average value being 7.4. Using this value, I calculate k_1' for each of the Tables 19 to 27.

$$k_1' \text{ calc} = k_1 + 7.4 \times (I_2) \times (H)^2 \times (I) \times 10^{13} \dots \dots (D)$$

The difference between the calculated and observed values of k_1' expressed as percent of the latter, is entered under "Diff." With the exception of Tables 22 and 23, the greatest discrepancy is 4 percent, well within the experimental errors. In the case Tables 22 and 23 the difference amounts to 10 percent; k_1' for Table 22 is, however, very uncertain (page 472), and if the average of k_1' for Tables 23 and 20 be entered instead of k_1' for each of them, the discrepancy between observed and calculated values of k_1' is reduced to 6 percent.

Representation of the results by a differential equation

$$dx/dt = k_1'(\text{IO}_3)/V \times 2.303 \dots\dots\dots (\text{p. 469})$$

$$k_1' = k_1 + 7.4 \times 10^9 \times (\text{I}_2) \times (\text{I}) \times (\text{H})^2 \times 1/V^4 \dots (\text{D, p. 470})$$

$$k_1 = \frac{K \times 1^{1.9} \times (\text{H})^2}{2.303 \times V^4} \dots\dots\dots (\text{B, p. 466})$$

$$\text{Let } R = 7.4 \times 10^9 \times 2.303 \dots\dots\dots (\text{E})$$

Then the general differential equation may be written

$$\frac{dx}{dt} = K \left(\frac{\text{IO}_3 - x}{V} \right) \left(\frac{\text{I} - y}{V} \right)^{1.9} \left(\frac{\text{H}}{V} \right)^2 + R \left(\frac{\text{IO}_3 - x}{V} \right) \left(\frac{\text{I} - y}{V} \right) \left(\frac{\text{I}_2}{V} \right) \left(\frac{\text{H}}{V} \right)^2 \dots\dots\dots (\text{F})$$

or more simply

$$\frac{dx}{dt} = (\text{IO}_3) \cdot (\text{I}) \cdot (\text{H})^2 \left\{ \frac{K(\text{I})^{0.9} + R(\text{I}_2)}{V^5} \right\} \dots\dots\dots (\text{G})$$

where

$$K = 2.54 \times 10^{10} \dots\dots\dots (\text{p. 467})$$

$$R = 1.70 \times 10^{10} \dots\dots\dots (\text{E})$$

TABLE 19

IO_3 , 0.000025; Iod, 40 cc; (I_2 , 0.00183; I , 0.002053);
HAc, 0.0058; NaAc, 0.0015; H , 0.000007

t	T_h	$k_1' \times 10^3$
2	11.85	41.3
4	10.04	38.6
6	8.75	36.0
		Av. 38.6

TABLE 20

IO_3 , 0.000025; Iod, 20 cc; (I_2 , 0.000915; I , 0.0010265);
 I , 0.000885; HAc, 0.0058; NaAc, 0.0015; H , 0.000007

t	T_h	$k_1' \times 10^3$
2	12.60	27.9
4	11.24	26.4
6	9.72	28.1
8	8.60	27.7
		Av. 27.6

TABLE 21

IO_3 , 0.000025; Iod, 10 cc; (I_2 , 0.000457; I , 0.0005133);
 I , 0.001328; HAc , 0.0058; NaAc , 0.0015; H , 0.000007

t	T_k	$k_1' \times 10^3$
2	12.97	21.7
4	11.66	23.4
6	10.20	24.6
8	9.05	24.9
		Av. 23.6

TABLE 22

IO_3 , 0.000025; Iod, 20 cc; (I_2 , 0.000915; I , 0.0010265);
 I , 0.000885; HAc , 0.0117; NaAc , 0.0015; H , 0.000014

t	T_k	$k_1' \times 10^3$
1	11.09	111.3
1.5	9.35	123.6
2	7.90	129.3
		Av. 121.4

TABLE 23

IO_3 , 0.000050; Iod, 20 cc; (I_2 , 0.000915; I , 0.0010265);
 I , 0.000885; HAc , 0.0058; NaAc , 0.0015; H , 0.000007

t	T_k	$k_1' \times 10^3$
1	26.58	31.3
2	24.51	32.8
3	23.94	(24.7)
4	22.20	27.7
		Av. 29.1

TABLE 24

IO_3 , 0.000025; Iod, 20 cc; (I_2 , 0.000915; I , 0.0010265);
 I , 0.002655; HAc , 0.0058; NaAc , 0.0015; H , 0.000007

t	$T\eta$	$k_1' \times 10^3$
1	12.99	73.8
1.5	10.70	(84.5)
2	10.00	78.1
3	8.17	81.5
		Av. 79.5

TABLE 25

IO_3 , 0.000025; Iod, 20 cc; (I_2 , 0.000915; I , 0.0010265);
 I , 0.000885; HAc , 0.0058; NaAc , 0.0030; H , 0.0000035

t	$T\eta$	$k_1' \times 10^3$
8	12.56	7.1
16	10.88	7.4
		Av. 7.3

TABLE 26

IO_3 , 0.000025; Iod, 10 cc; (I_2 , 0.000457; I , 0.0005133);
 I , 0.0030975; HAc , 0.0058; NaAc , 0.0015; H , 0.000007

t	$T\eta$	$k_1' \times 10^3$
1	12.24	68.5
2	10.09	76.2
3	8.62	73.5
4	7.51	70.2
		Av. 72.1

TABLE 27

IO_3 , 0.000025; Iod, 40 cc; (I_2 , 0.00183; I , 0.002053);
 I , 0.00177; HAc , 0.0058; NaAc , 0.0015; H , 0.000007

t	$T\eta$	$k_1' \times 10^3$
2	9.16	97.2

SERIES IV. SOLUTIONS OF HYDRIODIC AND IODIC ACIDS

Having determined the rates in solutions in which the components hydron, iodion, and iodation, could each be controlled separately, it remained to carry out a few measurements with the acids themselves.

The results of these experiments are given in Tables 28 to 34, where the symbols used have the significance explained on page 458. The concentrations are given on the assumption that hydriodic and iodic acids are completely dissociated into their ions. In order to keep the rate within measurable limits only small quantities of each reagent could be used; the experimental errors in this series are therefore much larger than in the previous tables; but nevertheless the constants are very fair.

Before performing the experiments with the pure acids, the measurements of Series I to III were connected with those of the following series, by several determinations in solutions containing (i) acetic acid, sodium acetate, potassium iodate, hydriodic acid, and (ii) acetic acid, sodium acetate, potassium iodide, iodic acid, respectively. The results were in good agreement with the requirements of equation (A) page 466, and demonstrated the absence of catalyzers in the hydriodic and iodic acid solutions.

In Tables 28 to 31 the hydriodic acid was present in excess; in Tables 32 to 34 the iodic acid. The values of K (page 466) for all these experiments are collected in Table 35; with the exception of K for Table 33, they show fair agreement. The laws which have been discovered in the systematic experiments of the previous series thus hold also for solutions containing hydriodic and iodic acids only. The average value of K however (0.84) is much lower than that found with acetic acid solutions (2.54).

A small part of this difference may be ascribed to the assumption of total dissociation of the acids made in the calculation. Experiments in which sodium chloride was added to the acid solution (Table 36), without effect on the rate, show that the difference cannot be ascribed to acceleration by the sodium

ions introduced with the sodium acetate in the previous series.

If it be assumed that the rate is strictly proportional to the square of the concentration of the hydrogen-ion, there remains only the hypothesis that the calculation of the dissociation of acetic acid is faulty. If in Table 17 H be set, not 0.000007 but 0.000012, the agreement is good; this corresponds to a value 0.00003 for the dissociation constant of acetic acid, however, which is entirely out of the question (see page 459). This is not the first time that the calculation of dissociation from conductivity measurements has given unsatisfactory results.

TABLE 28

IO_3 , 0.000005; I , 0.000564; H , 0.000569; Vol, 0.31 liter

t	As	$k_1 \times 10^3$
2	0.74	65.0
4	1.28	64.4
5	1.44	61.0
7	1.70	56.0
		Av. 61.6

TABLE 29

IO_3 , 0.000010; I , 0.000564; H , 0.000574; Vol, 0.31 liter

t	As	$k_1 \times 10^3$
2	1.51	67.3
3	2.06	65.5
4	2.33	57.5
		Av. 63.4

TABLE 30

IO_3 , 0.000005; I , 0.001128; H , 0.001133; Vol, 0.31 liter

t	As	$k_1 \times 10^3$
0.25	1.66	(1568.7)
0.5	2.30	1216.4
1.0	2.58	1010.0
		Av. 1113.2

TABLE 31

 IO_3 , 0.000005 ; I, 0.000564 ; H, 0.000569 ; Vol, 0.39 liter

t	As	$k_1 \times 10^3$
4	0.81	36.1
8	1.37	33.0
		Av. 34.6

TABLE 32

 IO_3 , 0.0000488 ; I, 0.0000566 ; H, 0.0001054 ; Vol, 0.1 liter

t	As	k_1
4	0.45	540
8	0.84	578
		Av. 559

TABLE 33

 IO_3 , 0.0000976 ; I, 0.0000556 ; H, 0.0001542 ; Vol, 0.1 liter

t	As	k_1
2	1.02	2984
3	1.35	2956
4	1.60	2899
		Av. 2946

TABLE 34

 IO_3 , 0.0000488 ; I, 0.0001132 ; H, 0.0001620 ; Vol, 0.1 liter

t	As	k_1
2	1.60	1100
3	2.28	1114
4	2.56	1064
		Av. 1093

TABLE 35

No.	<i>V</i>	$IO_3 \times 10^3$	$I \times 10^3$	$H \times 10^3$
28	0.31	5.0	564.0	569.0
29	0.31	10.0	564.0	574.0
30	0.31	5.0	1128.0	1133.0
31	0.39	5.0	564.0	569.0
32	0.10	48.8	56.6	105.4
33	0.10	97.6	56.6	154.2
34	0.10	48.8	113.2	162.0

No.	$k_1 \times 10^3$	k_2	$K \times 10^{-10}$
28	61.6	—	0.62
29	63.4	—	0.64
30	1113.2	—	0.82
31	34.6	—	0.70
32	—	559.0	1.00
33	—	2946.0	1.25
34	—	1093.0	0.83

Av. 0.84

TABLE 36

5 cc F/10 NaCl; IO_3 , 0.000005; I, 0.000564; H, 0.000569;
Vol, 0.31 liter

<i>t</i>	<i>As</i>	$k_1 \times 10^3$
2	0.75	66.0
4	1.22	60.4
5	1.43	60.2

Av. 62.2

TABLE 37

10 cc F/10 NaCl; IO_3 , 0.000005; I, 0.000564; H, 0.000569;
Vol, 0.31 liter

<i>t</i>	<i>As</i>	$k_1 \times 10^3$
2	0.70	61.0
4	1.21	60.0
5	1.45	61.4

Av. 60.8

**SERIES V. HYDRIODIC AND IODIC ACIDS, IODINE (TRI-IODION)
PRESENT IN EXCESS**

Tables 39 to 41 give the results of measurements with the solutions of hydriodic and iodic acids to which an excess of iodine was added in the form of hydrogen tri-iodide (HI_3). As the results of this series are in full agreement with those of Series III, I shall merely add the following table (38) to show that the effect of tri-iodion on the rate between the pure acids is governed by the same laws as its effect when in presence of neutral salts (sodium acetate and potassium salts in Series III). The meanings of the symbols are the same as in the tables of Series III. In order to facilitate comparison of Series V with Series IV, I have recalculated the corresponding values of k_1 in the former series for the same concentration of iodion as in Tables 39 to 41 (assuming that the rate is proportional to the square of the concentration of the iodion). These numbers are entered under k_1 .

TABLE 38

No.	$\text{IO}^3 \times 10^3$	$\text{I} \times 10^3$	$\text{H} \times 10^3$	$\text{I}_2 \times 10^3$
39	5	356	569	208
40	10	356	574	208
41	5	712	1133	416

No.	$k_1' \times 10^3$	$k_1 \times 10^3$	$(k_1' - k_1) \times 10^3$	S
39	67.0	25.0	42.0	1.7
40	59.5	25.3	34.2	1.4
41	882.0	443.0	439.0	1.2

Av. 1.4

The constancy of the quotient,

$$S = \frac{(k_1' - k_1) \times 10^{-12}}{(\text{I}_2) \times (\text{H})^2 \times (\text{I})} \dots\dots\dots (\text{H})$$

shows that the rate, in the presence of an excess of iodine, is proportional to the square of the concentration of the hydron, to the first power of that of the iodion and to the first power of that of the tri-iodion.

The results of Series IV and V may thus be represented by the differential equations (F) and (G), of page 471, which served for Series I-III; the numerical values of K and R however, are different.

$$K = 0.84 \times 10^{10} \text{ (instead of } 2.54 \times 10^{10}, \text{ page 471)}$$

$$R = 0.32 \times 10^{10} \text{ (instead of } 1.70 \times 10^{10}, \text{ page 471).}$$

TABLE 39

IO_3 , 0.00005; I , 0.00005; I_2 , 0.000208; H , 0.000569; Vol, 0.31

t	$T\hbar$	$k_1' \times 10^3$
1	2.37	81.7
2	2.15	62.0
2.5	1.90	71.0
5	1.33	66.5
7	1.20	54.0
		Av. 67.0

TABLE 40

IO_3 , 0.000010; I , 0.000356; I_2 , 0.000208; H , 0.000574; Vol, 0.31

t	$T\hbar$	$k_1' \times 10^3$
2	4.35	59.5
3	4.00	(52.0)
		Av. 59.5

TABLE 41

IO_3 , 0.000005; I , 0.000712; I_2 , 0.000416; H , 0.001133; Vol, 0.31

t	$T\hbar$	$k_1' \times 10^3$
0.5	1.13	807
0.75	0.59	914
1.0	0.34	925
		Av. 882

V. TEMPERATURE COEFFICIENT

The measurements of Table 1 (at 0° C) were repeated at a temperature of 37° C, and one measurement was made at 14° C. The results are given in Table 42.

TABLE 42

IO₃, 0.000025; I, 0.00177; HAc, 0.00585; NaAc, 0.0015;
H, 0.000007

Temp.	<i>t</i>	<i>As</i>	<i>k</i> ₁ × 10 ³	<i>k</i> × 10 ⁻¹⁰
37° C.	2	2.68	44.0	—
"	4	4.63	43.0	—
"	6	6.18	41.0	—
			Av. 42.6	5.90
14° C.	4	3.23	28.0	3.90
0° C.	—	—	18.3	2.54

The rate rises almost *linearly* with the temperature, a rise from zero to 10° C multiplying the rate by about 1.4. This is one of the lowest temperature coefficients on record.¹

VI. EFFECT OF LIGHT AND OF CATALYZERS

Experiments with solutions of hydriodic and iodic acids in which, by means of a concave mirror, direct sunlight was concentrated on the reacting mixture in the beaker, gave the same results as those carried out in the diffuse light of the laboratory.

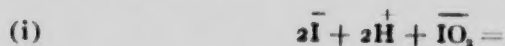
By means of a few measurements it was found that potassium bichromate does not affect the rate and that ferrous sulphate accelerates only moderately.

VII. MOLECULAR INTERPRETATION OF THE RESULTS

The form of the differential equation found above suggests the simultaneous occurrence of two reactions in solutions con-

¹ See DeLury. Jour. Phys. Chem. 7, 251 (1903).

taining iodide, iodate, acid and free iodine, corresponding to the chemical equations



in which the indices of the differential equations serve as coefficients.

The right-hand member of equation (i) may be filled in conjecturally thus,



giving HOI and its ion $\bar{OI}$ as the oxidation product of HI and reduction product of $\bar{IO}_3$ respectively. This assumption is in accordance with Roebuck's work on the reaction between arsenious acid and hydrogen iodide,¹ and with the current views on oxidation in organic chemistry, where the series of oxidation products of methyl alcohol, for instance, are regarded as derived from CH_4 by successive introduction of O between H and the electronegative element.

It is more difficult to invent a right-hand member for equation (ii); the following, however, might serve if it be supposed that the substance I_2OH (invented *ad hoc*) straightway decomposes into I_2 and IOH.



My thanks are due to Prof. W. Lash Miller, at whose suggestion this research was undertaken, and under whose supervision it has been carried out.

*The University of Toronto,
June, 1904.*

¹ Jour. Phys. Chem. 6, 365 (1902).

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